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**SUSCEPTIBILITY OF POLYURETHANE FOAM TO
DETERIORATION BY IMPURITIES OR CONTAMINANTS
IN ETHYLENE GLYCOL MONOMETHYL ETHER**

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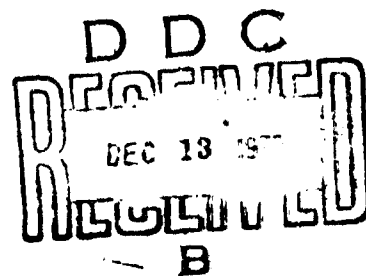
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**Air Force Aero Propulsion Laboratory
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Wright-Patterson Air Force Base, Ohio**

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FOREWORD

This is a joint report prepared by Monsanto Research Corporation, Dayton, Ohio, under Air Force Contract F33615-69-C-1325, and the Air Force Aero Propulsion Laboratory (AFAPL/SFF) of the Air Force Systems Command. The contract was initiated under Project 3048, "Aviation Fuels," Task No. 304805, "Hydrocarbon Fuels," and was administered under the direction of the Air Force Aero Propulsion Laboratory (AFAPL/SFF), Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Major J. T. Morgan and Capt. W. L. Noll as Project Engineers.

This report covers work conducted from 1 August 1969 to 15 September 1970 at the Dayton Laboratory of Monsanto Research Corporation and at the laboratory facilities of Wright-Patterson Air Force Base. It was submitted by the authors in October 1970. Contractor's identifying numbers are Project 2581 and Report No. MRC-DA-269. Co-authors of the report are G. W. Gandee of the Air Force Aero Propulsion Laboratory and W. G. Scribner of Monsanto Research Corporation. Additional technical assistance was provided by N. W. Mott, D. E. Kirk, R. R. Ferguson, F. N. Hodgson, J. V. Pustinger, R. J. Burton, G. Wheeler, C. E. Bowie, C. E. Lowe and R. E. Pence, all of the Monsanto Research Corporation staff.

Technical contributions to the program were also provided by R. A. Cupper, Union Carbide Corporation, T. O. Reed of the Deputy for Engineering, Aeronautical Systems Division, and Robert Voltz and W. H. Everman of the Foam Division of the Mott Paper Company.

This report has been reviewed and is approved.

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ABSTRACT

Polyurethane foam used to suppress fire and explosion in the fuel tanks of certain aircraft normally possesses excellent storage stability in ethylene glycol monomethyl ether (EGME) and water mixtures such as would be found in fuel tank water bottoms. However, certain lots of EGME were found to cause severe degradation of foam after one week of storage at 160°F in 25% EGME-75% water. A major supplier of EGME traced the cause of foam degradation to the presence of lead and/or tin at the ppm level in EGME, a condition resulting from the storage of EGME in one-gallon cans with soldered seams.

This report describes work which established that (1) the pH (4 to 7) of the exposure medium had no effect on the tensile strength of polyurethane foam; (2) certain organic impurities or contaminants in EGME did not cause foam degradation; and (3) glycerol provides no "protection" to foam specimens stored in EGME which degraded foam. Data are also presented which confirm the lead ion as the cause of foam degradation and which demonstrate that certain other metal ions at the ppm level did not produce the degradation effect under the solution conditions tested.

It is recommended that foam stability be studied employing typical water bottoms obtained from the field.

A mechanism for metal ion-catalyzed foam degradation via hydrolysis is suggested.

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I. INTRODUCTION

The Fuel System Icing Inhibitor (FSII) material used under MIL-I-27686D by the Air Force in all JP-4 fuel consisted of a combination of 99.6% (by vol) ethylene glycol monomethyl ether (EGME) and 0.4% (by vol) glycerol.

The formulation was designed to preclude aircraft fuel system icing conditions and, as a secondary benefit, to provide protection against microbiological contamination. The FSII, originally added at a concentration of 0.1% to 0.15% (by vol) to the fuel, has undergone several formulation modifications concerned with the glycerol constituent. The original role of the glycerol constituent in the 90-10 mixture was to protect the Buna-N topcoating in integral fuel tanks from any deterioration which could occur in the sump area where the water phase would build up an equilibrium concentration of FSII of about 25% (by vol). Almost immediately, the glycerol constituent was found to be insoluble in the fuel, and the percentage was reduced to 2% in lieu of 10%. After extensive tests were conducted, the glycerol constituent was reduced to 0.4% which represented the average solubility of material in jet fuel.

In the Spring of 1969, the Air Force Aero Propulsion Laboratory (AFAPL) initiated action to remove the glycerol constituent from the FSII specification MIL-I-27686. This action was the result of an extensive investigation which revealed that the percent glycerol in the water phase was considered ineffective in adding any protection to the Buna-N topcoating material (1). Also, a survey of the Air Force Logistics Command and discussions with the AF Materials Laboratory revealed that the potential problem of softening of the Buna-N coating by water bottoms in the sump areas of operational aircraft had been eliminated by coating the area at overhaul with the more resistant polyurethane material and specifying the urethane material in all new production aircraft. Finally it was found that at moderately low fuel temperature ($\sim 38^{\circ}\text{F}$), the glycerol portion of the FSII would be stripped from the fuel by the ground filter separator equipment, thus causing a premature removal of the filter due to a high pressure drop (2).

All government agencies were notified of this pending change. To assure that there were no detrimental effects on fuel system materials, the Aeronautical Systems Division requested that selected tests, required in the qualification of fuel system materials, be repeated with and without the presence of glycerol. One material receiving considerable attention at that time was the reticulated polyurethane foam produced by

Scott Paper, Foam Division. This material is used in combat aircraft as a passive defense measure to eliminate the fire and explosion threat due to hostile gunfire (3). In application, the foam conforming to MIL-B-8305⁴ completely fills the fuel tank and, therefore, can be exposed to the water phase of the sump area which contains the FSII.

A sample of the pure ethylene glycol monomethyl ether (EGME) was sent from AFAPL to Scott for the testing; the results of the 14-day exposure at 158°F indicated a severe loss in tensile strength after only 4 days of exposure. The initial conclusion was that the absence of the glycerol (0.1% in the aqueous solution) brought about failure of the foam specimens. Monsanto Research Corporation (MRC) was asked to run similar tests with a sample of FSII containing the glycerol. No problems were encountered. Therefore, a meeting was held at WPAFB on 17 September 1969 with Scott and MRC to resolve differences in procedures. General agreement was obtained that procedures, although slightly different, were not a factor and there was the possibility that a "bad" batch of EGME was involved. Further, an AFAPL in-house test conducted at 130°F with blocks of the foam in distilled water (25% aqueous solution of FSII and a 25% aqueous solution of EGME) did not appear to be physically affected after 45 days of exposure.

In order to check out the possibility of a "bad" batch of EGME, a program was outlined wherein samples from initially three and later five major suppliers were obtained and submitted to the foam test in accordance to ASTM procedures and conditions outlined by the Foam Specification. Four of the five EGME solutions (25% EGME and 75% water) passed the test; however, one supplier's material failed the test. Preliminary analysis failed to show any chemical difference which could account for this failure; therefore, an extensive testing program was initiated to determine the cause of the foam deterioration.

II. EXPERIMENTAL

A. TEST SOLUTIONS

Solutions for foam compatibility tests were prepared from various lots of ethylene glycol monomethyl ether or fuel system icing inhibitor listed in Table 1, by diluting 250 ml of the glycol ether or FSII to about one liter in a volumetric flask, cooling, and finally adjusting the volume to one liter.

Test solutions containing possible impurities or by-products were similarly prepared by adding a weighed portion of a reagent grade liquid or metal salt to a volumetric flask containing 250 ml of EGME and diluting to one liter.

The criterion for pass or failure of the foam material is described in MIL-B-83054. Requirements for foam specimens subjected to the test specified in this document are a minimum tensile stress at 200% elongation of 10 psi, a minimum tensile strength of 15 psi, and a minimum elongation of 250%.

B. STORAGE OF TEST SPECIMENS

The solutions were transferred to one quart wide-mouth bottles and were preheated overnight at $160 \pm 5^\circ\text{F}$. Two or more foam specimens were suspended from stainless steel racks, inserted into the preheated solution and maintained at the test temperature for one, two, or three weeks.

The foam specimens had been die cut by the Foam Division of the Scott Paper Company according to the drawing of "Die A" as per ASTM D 412-62T and were intended for use in the measurement of tensile stress at 200% elongation, ultimate tensile strength and ultimate elongation according to ASTM D 1564-T except that the initial jaw separation of the Instron was set at 2 in. as required in MIL-B-83054 (USAF) section 4.7.4.

At the completion of a test period, the specimens were dried @ 160°F for 3 hr and cooled for at least 30 min prior to tension testing according to ASTM D 1564-T.

Table 1

VARIOUS EGME SOLUTIONS
USED FOR FOAM COMPATIBILITY TESTS

<u>Sample</u>	<u>Compound</u>	<u>Origin</u>	<u>Date</u>	<u>Container</u>
A-1	EGME	APFF	12/69	5-gal drum
B-1	EGME	APFF	12/69	5-gal drum
B-2	EGME	MRC	10/69	Glass
C-1	EGME	APFF	12/69	5-gal drum
C-2	EGME	MRC	10/69	1-gal can
C-3	EGME	APFF	12/69	1-gal can
D-1	EGME	APFF	12/69	5-gal drum
D-2	EGME	MRC	10/69	Glass
E-1	EGME	APFF	11/69	5-gal drum

III. EXAMINATION OF EGME FROM VARIOUS SUPPLIERS

One gallon samples of commercial ethylene glycol monomethyl ether (EGME) were obtained from three suppliers and portions were mixed with distilled water to give solutions containing 75 vol % water - 25 vol % EGME. Foam specimens were placed in the solutions and were stored at 160°F for 7 days. Samples of undiluted EGME containing dumbbell specimens were also stored. After 7 days the specimens were removed from the test solutions and tested according to ASTM D 1564. Results are presented in Table 2.

The data indicate no significant loss in tensile strength of the specimens stored in 25 vol % B-2 and 25 vol % D-2, and a severe loss in tensile strength of the specimens stored in 25 vol % C-2. The data obtained with the 25 vol % C-2 were confirmed with a second series of tests.

A loss in tensile strength was also observed for all specimens stored in each undiluted EGME. These specimens swelled appreciably during the test. Interestingly, each of these specimens showed a significant increase in % elongation at ultimate psi.

Certain specification tests and instrumental analyses were performed on B-2, C-2, and D-2 in an effort to uncover chemical differences which could account for the behavior of C-2. However, glycol content, acid number, refractive index, gas chromatography, and nuclear magnetic resonance studies of several commercial EGME samples did not reveal why 25% aqueous C-2 was the only test fluid to produce foam specimens which broke before reaching 200% elongation when tested according to ASTM D 1564.

<u>Property</u>	<u>Requirement</u>	<u>B-2</u>	<u>C-2</u>	<u>D-2</u>
Acid Number	0.09 mg KOH/g, max	0.01	0.02	-
Ethylene Glycol	0.025 wt %, max	0.001	0.006	0.003
Refractive Index	-	1.4007	1.4007	1.4006
pH, 25% Solution	-	7.09	6.42	6.99

In an effort to secure a larger quantity of EGME affecting the tensile strength of polyurethane foam, to determine if another sample from supplier C would behave similarly to C-2, and to examine material from other suppliers, five-gallon samples of EGME from five of ten suppliers were obtained.

Tensile specimens were stored in 25.0 vol % aqueous EGME and also 24.9 vol % EGME plus 0.10 vol % glycerol. Six specimens

Table 2

TENSILE STRENGTH OF SCOTT FOAM STORED IN EGME
FROM THREE SUPPLIERS

Jaw Separation of Instron - 2 in.

7 Days @ 160°F

Sample	Initial	pH Final	Tensile Stress @ 200% Elongation (psi)	Ultimate Tensile Strength (psi)	% Elongation
Controls			15.1 14.8 14.0 14.8 13.2 <u>14.4</u>	24.3 23.5 20.9 22.8 21.3 <u>22.6</u>	350 330 320 330 320 <u>330</u>
			Avg		
B-2			9.2 9.3 9.6 <u>9.4</u>	21.3 17.6 23.2 <u>20.7</u>	440 380 440 <u>420</u>
			Avg		
25 vol % B-2	7.09	6.00	14.5 14.8 13.6 <u>14.3</u>	21.0 24.1 21.8 <u>22.3</u>	310 340 330 <u>330</u>
			Avg		
C-2			7.1 6.8 6.7 <u>6.9</u>	14.5 13.2 14.1 <u>13.9</u>	460 450 500 <u>470</u>
			Avg		
25 vol % C-2	6.42	4.97	- - - <u>-</u>	8.3 7.9 7.4 <u>7.9</u>	170 140 130 <u>150</u>
			Avg		
C-2			6.8 5.8 6.3 <u>6.3</u>	13.0 12.0 12.0 <u>12.3</u>	470 490 460 <u>470</u>
			Avg		
25 vol % C-2			- - - <u>-</u>	8.6 9.0 9.4 <u>9.0</u>	170 170 170 <u>170</u>
			Avg		

Table 2 - (cont'd)

<u>Sample</u>	<u>pH</u>		<u>Tensile Stress @ 200% Elongation (psi)</u>	<u>Ultimate Tensile Strength (psi)</u>	<u>% Elongation</u>
	<u>Initial</u>	<u>Final</u>			
D-2			7.4	16.0	460
25 vol % D-2	6.99	5.92	13.9	22.3	350
			13.2	19.7	330
			<u>14.7</u>	<u>22.7</u>	<u>340</u>
			Avg 13.9	21.6	340

were then placed in each test solution. Three specimens were removed after 7 days and three after 14 days and tested according to ASTM D 1564. Results presented in Table 3 indicate no significant loss in tensile strength of the foam specimens after 7 or 14 days.

In an attempt to isolate the cause of specimen failure, several additional exposures were performed. These included a study of the effect of pH of test solutions and an examination of distilled C-2. Aqueous buffered solutions of pH 4.00, 5.00, 6.00, and 7.00 were prepared from appropriate mixtures of 0.1M citric acid and 0.1M disodium hydrogen phosphate. Solutions were also prepared from C-2 (25.0 vol % aqueous; C-2, 24.9 vol % plus 0.10 vol % glycerol; distilled C-2, 25.0 vol % aqueous) and the pot residue from the distillation of C-2. The residue, 17 ml, was diluted to 250 ml with B-2 and finally diluted to 1000 ml with distilled water. The resulting solution, therefore, was 1.7 vol % in C-2 residue and 23.3 vol % in B-2. [B-2 did not adversely affect the tensile strength of foam specimens. (Table 2).]

The solutions were preheated for 24 hr at 160°F. Five specimens were then placed in each test solution. Three specimens were removed after 7 days, one after 14 days, and finally, one after 21 days. In each case, specimens were dried for 3 hr at 160°F, cooled for 30 minutes, and tested according to ASTM D 1564. Three control specimens were also tested for tensile strength.

The test data are presented in Table 4. The following conclusions are apparent from the data:

1. Storage of foam specimens in aqueous buffered solutions of pH 4.00, 5.00, 6.00, or 7.00 for 21 days did not result in a significant loss of tensile strength.
2. Distillation of C-2 yields a distillate which did not adversely affect the tensile strength of foam specimens stored for 21 days at 160°F.
3. The residue from the distillation of C-2 diluted in water to the 1.7 vol % level and also containing 23.3 vol % of an innocuous EGME caused severe loss in tensile strength of foam specimens in 7 days.
4. Earlier results on C-2 were confirmed. Aqueous solutions at the 25 vol % level caused severe loss in tensile strength of foam specimens in 7 days.
5. The addition of 0.10 vol % glycerol to the same EGME did not provide "protection" to the foams. Specimens still showed severe loss in tensile strength after 7 days.

Table 3

TENSILE STRENGTH OF SCOTT FOAM STORED IN EGME
FROM FIVE SUPPLIERS

Jaw Separation of Instron - 2 in.

Sample	Tensile Stress @ 200% Elongation (psi)	Ultimate Tensile Strength (psi)	% Elongation
<u>Controls</u>	11.6	21.6	430
	11.2	20.0	390
	11.4	23.4	450
Avg	<u>11.4</u>	<u>21.7</u>	<u>420</u>
<u>Distilled Water</u>	12.4	18.1	330
Initial pH 6.20	12.3	20.3	360
7 days	12.2	23.3	420
	<u>12.3</u>	<u>20.6</u>	<u>370</u>
Avg			
14 days	11.1	16.5	330
Final pH 5.70	11.9	21.2	380
	11.8	19.4	380
Avg	<u>11.6</u>	<u>19.0</u>	<u>360</u>
<u>A-1</u>			
25.0 vol % aqueous	11.2	18.7	360
Initial pH 5.91	11.4	19.9	410
7 days	12.8	22.6	390
	<u>11.8</u>	<u>20.4</u>	<u>390</u>
Avg			
14 days	11.6	20.3	400
Final pH 5.76	11.0	17.8	370
	11.0	20.8	440
Avg	<u>11.2</u>	<u>19.6</u>	<u>400</u>
24.9 vol % A-1 + 0.10 vol % Glycerol	11.4	22.7	450
Initial pH 5.98	11.4	21.2	410
7 days	11.3	21.8	430
	<u>11.4</u>	<u>21.9</u>	<u>430</u>
Avg			
14 days	11.1	19.6	410
Final pH 6.19	11.4	21.0	420
	11.6	19.6	380
Avg	<u>11.4</u>	<u>20.1</u>	<u>400</u>

Table 3 - (cont'd)

Sample	Tensile Stress @ 200% Elongation (psi)	Ultimate Tensile Strength (psi)	% Elongation
<u>B-1</u>			
25.0 vol % aqueous	11.6	18.3	370
Initial pH 5.19	11.5	20.2	390
7 days	12.8	23.4	410
	Avg 12.0	20.6	390
14 days	11.2	18.9	380
Final pH 5.78	11.5	20.2	390
	11.2	19.1	390
	Avg 11.3	19.4	390
24.9 vol % B-1 + 0.10 vol % Glycerol:	12.5	18.5	330
Initial pH 5.00	12.0	20.2	370
7 days	11.9	20.2	370
	Avg 12.1	19.6	360
14 days	11.5	21.7	420
Final pH 5.82	12.4	21.3	390
	11.7	20.4	410
	Avg 11.9	21.1	410
<u>C-1</u>			
25.0 vol % aqueous	11.5	21.0	390
Initial pH 5.98	11.5	20.4	410
7 days	11.3	23.3	460
	Avg 11.4	21.6	420
14 days	11.3	23.6	460
Final pH 5.68	11.5	21.7	430
	11.6	22.8	440
	Avg 11.5	22.7	440
24.9 vol % C-1 + 0.10 vol % Glycerol	11.6	21.6	430
Initial pH 5.92	11.2	20.0	390
7 days	11.4	23.4	450
	Avg 11.4	21.7	420
14 days	11.3	21.0	400
Final pH 5.62	10.4	18.2	400
	10.8	22.9	460
	Avg 10.8	20.7	420

Table 3 - (cont'd)

Sample	Tensile Stress @ 200% Elongation (psi)	Ultimate Tensile Strength (psi)	% Elongation
D-1			
25 vol % aqueous	11.6	22.3	420
Initial pH 6.95	11.9	22.6	420
7 days	11.6	18.5	380
	Avg 11.7	21.1	410
14 days	12.3	23.5	430
Final pH 4.99	12.1	20.7	390
	11.7	20.8	390
	Avg 12.0	21.7	400
24.9 vol % D-1 + 0.10 vol % Glycerol	10.3	19.3	430
Initial pH 7.07	12.1	21.3	400
7 days	10.5	18.5	400
	Avg 11.0	19.7	410
14 days	11.1	22.4	440
Final pH 5.07	12.0	20.7	390
	10.9	18.8	410
	Avg 11.3	20.6	410
E-1			
25.0 vol % aqueous	11.5	21.5	430
Initial pH 4.38	11.9	22.4	440
7 days	11.9	22.5	410
	Avg 11.8	22.1	430
14 days	10.8	20.0	430
Final pH 4.03	12.2	19.1	360
	11.6	20.0	380
	Avg 11.5	19.7	390
24.9 vol % E-1 + 0.10 vol % Glycerol	11.3	18.7	370
Initial pH 4.32	11.8	21.8	410
7 days	12.2	22.4	400
	Avg 11.8	21.0	390
14 days	10.7	13.8	310
Final pH 3.98	11.2	18.2	380
	11.9	20.8	410
	Avg 11.3	17.6	370

To provide sufficient material for analysis, an additional sample of C-2 was obtained on 19 December 1969. Three specimens were stored for one week in a 25.0 vol % solution of this sample (C-3). Curiously, the data (Table 4) indicate that this new sample did not cause loss in tensile strength of the specimens. However, when this lot of EGME was tested in duplicate at a later date (after storage in the original sample container at room temperature for two months), it was then found to cause severe loss of tensile strength of foam specimens (Table 4). Furthermore, the degrading component could be concentrated in the last 10% of a distillation as was found with C-2. An explanation for this effect is provided in Section V.

Table 4

TENSILE STRENGTH OF SCOTT FOAM
STORED IN AQUEOUS BUFFERED SYSTEMS
AND CERTAIN EGME SOLUTIONS

Jaw Separation of Instron - 2 in.

	Tensile Stress @ 200% Elongation (psi)	Ultimate Tensile Strength (psi)	% Elongation
<u>Initial pH 4.00</u>	15.6	22.1	300
7 days	13.2	20.0	315
	15.8	24.1	320
Avg	14.9	22.1	310
14 days	12.0	21.0	370
21 days	12.2	14.7	260
Final pH 4.05			
<u>Initial pH 5.00</u>	16.2	24.0	315
7 days	15.1	20.3	290
	14.8	19.2	280
Avg	15.4	21.2	295
14 days	12.0	22.0	420
21 days	12.2	17.5	350
Final pH 5.12			
<u>Initial pH 6.00</u>	13.2	18.9	300
7 days	14.5	22.7	330
	14.5	19.3	280
Avg	14.1	20.3	300
14 days	13.0	20.0	360
21 days	12.4	18.4	320
Final pH 6.09			
<u>Initial pH 7.00</u>	14.2	22.5	330
7 days	15.4	22.2	310
	15.6	25.1	340
Avg	15.1	23.3	330
14 days	12.0	21.0	390
21 days	13.2	22.9	380
Final pH 7.06			

Table 4 - (Cont'd)

Sample	Tensile Stress @ 200% Elongation (psi)	Ultimate Tensile Strength (psi)	% Elongation
<u>Controls</u>	14.1	19.0	280
	16.8	25.1	330
	15.4	20.0	270
Avg	<u>15.4</u>	<u>21.4</u>	<u>290</u>
<u>Distilled C-2</u>	13.7	20.5	310
<u>Initial pH 6.65</u>	13.6	21.3	320
7 days	14.5	23.6	330
Avg	<u>13.9</u>	<u>21.8</u>	<u>320</u>
14 days	11.0	22.0	430
21 days	12.2	19.5	340
Final pH 6.03			
<u>Pot Residue From</u>			
<u>Distillation of C-2</u>	-	5.1	100
<u>Initial pH 6.52</u>	-	7.6	150
7 days	-	3.9	70
Avg	-	<u>5.5</u>	<u>110</u>
14 days	-	3.4	33
21 days		Disintegrated	
Final pH 5.20			
<u>C-2 + 0.10 vol % Glycerol</u>	-	6.2	120
<u>Initial pH 6.20</u>	-	6.6	140
7 days	-	5.3	100
Avg	-	<u>6.0</u>	<u>120</u>
14 days	-	3.1	33
21 days	-	2.1	30
Final pH 4.90			
<u>C-2</u>	-	5.8	100
<u>Initial pH 6.21</u>	-	7.1	140
7 days	-	5.4	100
Avg	-	<u>6.1</u>	<u>110</u>
14 days	-	2.9	40
21 days	-	1.7	20
Final pH 5.09			

Table 4 - (Cont'd)

<u>Sample</u>	<u>Tensile Stress @ 200% Elongation (psi)</u>	<u>Ultimate Tensile Strength (psi)</u>	<u>% Elongation</u>
<u>C-3 Supplied 12-19-69</u>	12.3	17.3	290
<u>Initial pH 6.71</u>	11.9	16.5	300
7 days	13.2	25.8	340
	Avg 12.5	20.5	310
Final pH 5.59			
<u>C-3 Stored in Original Container for 2 Months</u>	-	5.3	130
<u>Initial pH 6.50</u>	-	6.0	150
Final pH 5.14	Avg -	5.7	140
<u>Residue From Distillation, 1.5%; B-1, 23.5%</u>	8.2	8.2	200
<u>Initial pH 6.22</u>	7.6	7.7	220
	Avg 7.9	8.0	210
Final pH 5.30			
<u>Residue From Distillation, 0.1%; B-1, 24.9%</u>	12.5	22.5	390
<u>Initial pH 5.50</u>	12.7	22.9	390
	Avg 12.6	22.7	390
Final pH 4.69			

IV. EFFECT OF POSSIBLE TRACE IMPURITIES IN EGME

Ethylene glycol monomethyl ether is commercially prepared by the addition of methyl alcohol to ethylene oxide in the presence of sulfuric acid (4).



The reaction could be accompanied by the formation of higher homologs or other impurities most of which are removed by distillation of the reaction mixture.

In an effort to establish the reason why certain lots of EGME cause loss of tensile strength of polyurethane foam, various possible starting materials or by-products of the commercial preparation of EGME were examined. These compounds were added at the 0.5 vol % level to aqueous solutions containing 25 vol % B-1 or B-2. Two foam specimens were stored for one week at 160°F in these solutions and subsequently tested by ASTM D 1564. Results presented in Table 5 indicate that ethylene glycol, hydrogen peroxide, methanol, formaldehyde, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether do not adversely affect the tensile strength at the concentration tested.

Table 5

EFFECT OF VARIOUS ORGANIC COMPOUNDS ON THE TENSILE
STRENGTH OF SCOTT FOAM STORED IN EGME

Jaw Separation of Instron - 2 in.

<u>Sample</u>	<u>Tensile Stress @ 200% Elongation (psi)</u>	<u>Ultimate Tensile Strength (psi)</u>	<u>% Elongation</u>
<u>Ethylene Glycol Dimethyl</u>			
Ether, 0.5 vol %;	12.0	22.5	440
B-2, 24.5 vol %	11.7	20.8	400
Initial pH 6.22	Avg 11.9	21.7	420
Final pH 4.17			
<u>Diethylene Glycol Dimethyl</u>			
Ether, 0.5 vol %;	12.8	20.2	350
B-2, 24.5 vol %	12.0	21.8	410
Initial pH 5.80	Avg 12.4	21.0	380
Final pH 4.13			
<u>Methanol, 0.5 vol %;</u>			
B-1, 24.5 vol %	12.3	21.9	390
Initial pH 5.39	12.2	17.8	340
Final pH 4.61	Avg 12.3	19.9	370
<u>Formaldehyde, 0.5 vol %;</u>			
B-1, 24.5 vol %	12.4	19.0	340
Initial pH 4.67	13.0	20.2	350
Final pH 4.28	Avg 12.7	19.6	350
<u>Hydrogen Peroxide, 0.5</u>			
<u>vol %; B-1, 24.5 vol %</u>	11.8	15.4	290
Initial pH 4.89	11.0	15.9	320
Final pH 2.80	Avg 11.4	15.7	310
<u>Ethylene Glycol, 0.1 vol %;</u>			
B-1, 24.9 vol %	11.2	17.9	360
Initial pH 4.82	11.4	19.0	370
	Avg 11.3	18.5	365

V. EFFECT OF METAL IONS

At this stage of the investigation, the assistance of the technical service department of one of the major suppliers of EGME was requested. The Research and Development Department of Union Carbide Corporation agreed to assist, and they were provided with all background information on the problem. Data on a "bad" sample proved to be an important clue. This sample initially did not influence the tensile strength of foam. However, after storage for two months in a one-gallon tinned container, the sample severely degraded foam specimens stored for one week at 160°F.

The Union Carbide investigator to whom the foam problem was referred was aware of work at another Union Carbide laboratory which demonstrated that high tin and lead contents (~ 100 ppm) were present in EGME stored in one-gallon tinned cans. He therefore suspected that lead and/or tin in EGME (derived from storage of EGME in cans) was the cause of severe loss of tensile strength of foam. This hypothesis was confirmed experimentally (5) by examination of samples stored for one month in one-gallon cans. After storage, the samples, which contained 50 ppm Sn and 65 ppm Pb, were found to severely degrade polyurethane foam. Control samples stored in glass contained no detectable lead or tin and did not produce tensile strength failure of foam specimens.

It was considered worthwhile to confirm the effect of lead and/or tin ions, to establish the minimum concentration required to produce tensile strength failure, and to study the effect of other metal ions which might be expected to be present in an aircraft water bottom.

The following solutions were prepared employing 25 vol % EGME:

- 250 ppm lead(II) added as lead acetate, unbuffered
- 96 ppm lead(II) added as lead acetate, unbuffered
- 25 ppm lead(II) added as lead acetate, unbuffered
- 250 ppm lead(II) added as lead nitrate, buffered
- 250 ppm lead(II) added as lead perchlorate, unbuffered
- 100 ppm tin(II) added as tin(II) chloride, buffered
- 100 ppm tin(IV) added as tin(IV) chloride, buffered
- 100 ppm copper(II) added as copper sulfate, unbuffered
- 100 ppm iron(III) added as iron sulfate, buffered
- 100 ppm zinc(II) added as zinc sulfate, unbuffered
- 100 ppm aluminum(III) added as aluminum sulfate, buffered

Solutions indicated as having been buffered were treated with 1M sodium acetate to yield a pH between 5 and 6. Unbuffered

solutions had an initial pH within the desired range and were not treated further.

The solutions were preheated in an oven overnight, and two foam specimens were added to each solution. After storage at 160°F for seven days, the foam specimens were removed and tested according to ASTM D 1564.

Results are presented in Table 6. The conclusions are:

1. Lead ion at the 25 ppm level (such as would result from preparation of a 25 vol % solution of EGME containing 100 ppm Pb) causes loss of tensile strength of foam. Lead ion at the 250 ppm level disintegrates the foam during one week at 160°F.
2. The lead ion must be essentially uncomplexed or the effect will not be observed. For example, in 250 ppm solution of lead acetate, wherein 87% of the lead is present as Pb(II) and 13% is present as $\text{Pb(CH}_3\text{COO)}^+$ (6), the effect is observed. Similarly, the effect is observed in a solution of lead perchlorate. The perchlorate ion is a noncomplexing anion (7). However, the effect is not observed in a lead solution to which a high concentration of acetate ion is added, yielding undissociated or even negatively charged complex species. [Lead ion at the 10^{-3}M level in a solution which is also 1M in acetate exists principally as $\text{Pb(CH}_3\text{COO)}_2^-$ (76%) and undissociated $\text{Pb(CH}_3\text{COO)}_2$ (21%) (6).]
3. Copper and zinc at the 100 ppm level do not promote loss of tensile strength of foam. Tin(II), tin(IV), iron, and aluminum at the same level also do not produce loss of tensile strength. However, the tests were performed with buffered solutions and extensive hydrolysis was observed.

Table 6

EFFECT OF METAL IONS ON THE TENSILE STRENGTH
OF SCOTT FOAM STORED IN EGME

Sample	Tensile Stress @ 200% Elongation (psi)	Ultimate Tensile Strength (psi)	% Elongation
Control	17.6 16.6 <u>15.5</u>	21.4 21.9 <u>19.7</u>	290 280 <u>290</u>
	Avg	16.6 <u>21.0</u>	290
<u>Pb(II)</u> , 250 ppm (Lead Acetate, unbuffered) Initial pH 6.25 Final pH 5.08	Disintegrated		
<u>Pb(II)</u> , 96 ppm (Lead Acetate, unbuffered) Initial pH 6.04 Final pH 5.14	- - <u>-</u>	2.7 3.4 <u>3.1</u>	40 50 <u>45</u>
	Avg	-	-
<u>Pb(II)</u> , 25 ppm (Lead Acetate, unbuffered) Initial pH 6.15 Final pH 5.29	8.8 9.4 <u>9.1</u>	8.8 11.6 <u>10.2</u>	200 220 <u>210</u>
	Avg	-	-
<u>Pb(II)</u> , 250 ppm (Lead Nitrate, buffered) Initial pH 5.00 Final pH 4.79	12.3 12.2 <u>12.3</u>	19.5 21.1 <u>20.3</u>	330 370 <u>350</u>
	Avg	-	-
<u>Pb(II)</u> , 250 ppm (Lead Perchlorate) Initial pH 6.29 Final pH 4.80	- - <u>-</u>	6.0 6.4 <u>6.2</u>	140 140 <u>140</u>
	Avg	-	-
<u>Sn(II)</u> , 94 ppm (Tin (II) Chloride, buffered) Initial pH 5.90 Final pH -	13.9 15.0 <u>14.5</u>	21.0 22.7 <u>21.9</u>	300 340 <u>335</u>
	Avg	-	-
<u>Sn(IV)</u> , 98 ppm (Tin (IV) Chloride, buffered) Initial pH 5.76 Final pH 5.73	14.7 15.0 <u>14.9</u>	21.6 20.4 <u>21.0</u>	340 300 <u>320</u>
	Avg	-	-

Table 6 (Cont'd)

Sample	Tensile Stress @ 200% Elongation (psi)	Ultimate Tensile Strength (psi)	% Elongation
<u>Copper(II)</u> , 100 ppm (Copper Sulfate, unbuffered) Initial pH 5.00 Final pH 3.73	12.3 13.4 Avg 12.9	19.3 18.9 19.1	330 310 320
<u>Iron(III)</u> , 100 ppm (Iron Sulfate, buffered) Initial pH 5.00 Final pH 4.85	13.1 10.4 Avg 11.8	22.5 18.7 20.6	370 350 360
<u>Zinc(II)</u> , 100 ppm (Zinc Sulfate, unbuffered) Initial pH 5.70 Final pH 4.90	14.1 12.7 Avg 13.4	22.2 20.3 21.3	340 350 350
<u>Aluminum(III)</u> , 100 ppm (Aluminum Sulfate, buffered) Initial pH 5.00 Final pH 4.85	12.7 13.4 Avg 13.1	17.1 21.1 19.1	310 340 330

VI. SUMMARY AND DISCUSSION

Lead and/or tin derived from one-gallon cans by EGME on storage at ambient temperature causes the degradation of polyurethane foam stored in 25% EGME-75% water solutions at 160°F in 7 days or less. The effect of lead ion can also be simulated by the addition of lead as lead acetate or perchlorate to "good" EGME.

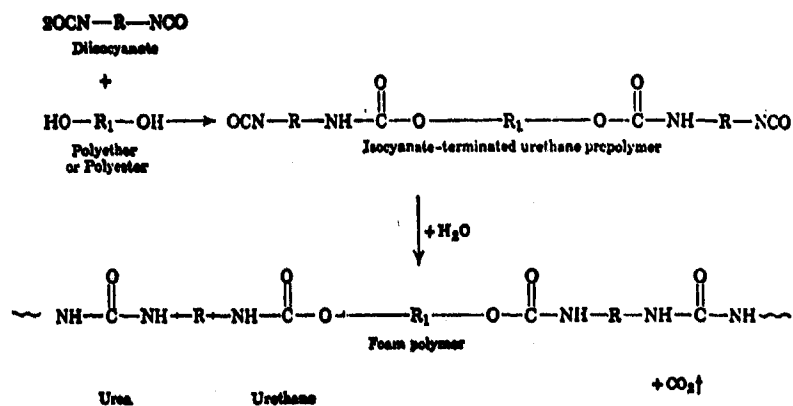
Tin(II), tin(IV), iron(III), and aluminum(III) when deliberately added at the ppm level to EGME solutions did not cause specimen failure. However, these ions were extensively hydrolyzed under the test conditions (pH ~5) and may not have been in the proper ionic form to catalyze or otherwise cause foam degradation.

Certain of these and other metal ions, which have on occasion been found in contaminated water bottoms, may very well have the ability to cause foam degradation. It is suggested that this aspect of the foam stability problem be investigated.

The mechanism of metal ion-promoted degradation is not yet established. Possibilities are oxidative degradation and hydrolysis. Oxidative degradation of polyether foams has been demonstrated for certain types of tin catalysts (dialkyl tin compounds) under severe temperature conditions (8). In these cases, degradation was attributed to alkyl radicals which initiated the oxidation process. However, in the case of foams stored in EGME-water systems, it would seem that hydrolysis would be the more likely route.

Hydrolysis results in the breaking of polymer chains thereby decreasing the average molecular weight per cross-link. Eventually, the average molecular weight might reach the range where properties such as tensile strength begins to fall off sharply with further decreases in molecular weight (9).

The formation of a prepolymer and the subsequent foaming reaction can be represented schematically (10):



It is speculated that metal ions such as lead which exhibit a preference for metal-oxygen bond formation might interact with carbonyl groups of the urethane linkages, thereby weakening the amide-carbon or ester-carbon bonds and causing them to be susceptible to hydrolysis.

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13. ABSTRACT Polyurethane foam used to suppress fire and explosion in the fuel tanks of certain aircraft normally possesses excellent storage stability in ethylene glycol monomethyl ether (EGME) and water mixtures such as would be found in fuel tank water bottoms. However, certain lots of EGME were found to cause severe degradation of foam after one week of storage at 160°F in 25% EGME-75% water. A major supplier of EGME traced the cause of foam degradation to the presence of lead and/or tin at the ppm level in EGME, a condition resulting from the storage of EGME in one-gallon cans with soldered seams. This report describes work which established that (1) the pH (4 to 7) of the exposure medium had no effect on the tensile strength of polyurethane foam; (2) certain organic impurities or contaminants in EGME did not cause foam degradation; and (3) glycerol provides no "protection" to foam specimens stored in EGME which degraded foam. Data are also presented which confirm the lead ion as the cause of foam degradation and which demonstrate that certain other metal ions at the ppm level did not produce the degradation effect under the solution conditions tested. It is recommended that foam stability be studied employing typical water bottoms obtained from the field. A mechanism for metal ion-catalyzed foam degradation via hydrolysis is suggested.		

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